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(54) Title: **TREATMENT OF ENVIRONMENTAL POLLUTANTS WITH MINERAL ORES**

(57) **Abstract:** A method for removing a pollutant from emissions or the environment comprising: contacting a mineral ore or the use of a mineral ore selected from the group consisting of bauxite, modified bauxite and mixtures thereof. Typically, the pollutant is a heavy metal or a microorganism.

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TREATMENT OF ENVIRONMENTAL POLLUTANTS WITH MINERAL ORES

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This application claims the benefits of U.S. Provisional Patent Application No. 60/363,693, filed March 12, 2002; and U.S. Provisional Patent Application No. 60/396,526, filed July 17, 2002. The entire text and drawings of the 10 above mentioned provisional applications are hereby incorporated herein by reference as if completely rewritten herein.

FIELD OF THE INVENTION

The present invention discloses the use of several relatively raw 15 materials including bauxite, iron ore (e.g. magnetite, hematite, goethite), feldspar, lignite and mixtures thereof for the amelioration of environmental pollutants and/or emissions. Typical pollutants in the emissions or the environment include heavy metals such as arsenic, cadmium, chromium, nickel, mercury; microorganisms; organic solvents; and the like.

20

BACKGROUND OF THE INVENTION

Pollutants in or on the ground, or in surface or ground waters pose an increasing threat to the environment. The pollutants may result from 25 industrial discharges, accidental spills, mine drainage, mine tailing seepage or leaks and the like. Typically, large quantities of polluted materials need to be treated so that cost of the treating materials becomes an important factor. The present invention seeks to answer this need by using low cost, readily available materials to bind the pollutants.

Heavy metals, such as mercury, arsenic, cadmium, chromium, and 30 selenium, are used in a number of manufacturing operations and industrial and consumer products, but are hazardous to human health and the ecosystem when released to the environment. Often, heavy metals have to be removed from gas, water, or soil streams exiting a manufacturing facility

describes a process for filtering fine particulates from a stream of hot gas by blending a fraction of particles removed by the cyclones back to the gas; this work mentions the use of diatomite or bauxite particles that can be blended into the gas stream to remove corrosive sodium and potassium vapors. U.S.

- 5 Pat. No. 3,917,733 describes a two-step process for removing halogen-containing chemicals from a liquid hydrocarbon stream by using alumina or bauxite as adsorbents, and then using the spent liquid-stream adsorbents as adsorbents for treating gas streams. In all these applications, bauxite in an activated form (following heat treatment to 400 °C or above) is used primarily
10 as an adsorbent, rather than in a raw or gently modified form as a catalyst to cause transformations of the target gas stream.

Many of these previous processes suffer from one or more of the following limitations:

- 15 1. The use of the reagent generates a waste product that interferes with its eventual reuse or disposal.
2. The reagent is too specific towards one or other target pollutant
3. A two-step process is required to obtain adequate removal of the pollutant metals. This increases the complexity of the process and cost of the
20 treatment.
4. The reagent is relatively expensive and economic use of the reagent requires another process to regenerate and reuse the reagent.

The present invention addresses these limitations. The invention consists of a reagent that is commonly available, removes multiple pollutants,
25 is relatively cheap and can therefore be disposed of after a single use.

BRIEF DESCRIPTION OF THE INVENTION

A process for treating gas, water, or soil containing heavy metals to prevent their migration in the environment is disclosed. The process involves contacting the
30 heavy metals with a multi-functional sequestration agent, namely, bauxite or modified bauxite. Bauxite is used in its relatively natural form (except for appropriate size reduction to fit a particular application) or in modified form (for

The bauxite can be either be placed as granular material in a trench, or injected as a powder into deeper aquifers.

Figure 4(a) shows the mixing of bauxite with surface soils to sequester pollutants. Figure 4(b) shows the placement of bauxite on top of

- 5 contaminated sediments to prevent migration of pollutants to the water body above.

Figure 5 shows that the pollutant removal of bauxite can be sustained long enough for the treatment to be economical.

10 **DETAILED DESCRIPTION OF THE INVENTION AND BEST MODE**

Broadly the invention include a process for treatment of heavy metals using a multi-functional sequestration agent

One embodiment of the invention consists of the use of bauxite, a common aluminum ore material, for sequestration of pollutant metals from

- 15 gaseous phase (like flue gas), aqueous phase (surface water or groundwater), and solid phase (like soil or subsurface materials). The bauxite is used as its natural form or in a modified form that still retains the essential character of the bauxite. Modifications may include, but are not limited to, simple processes, such as wetting with water, mild heating to temperatures below
20 300 °C, and/or soaking in solutions of common acids, bases, or salts. The modifications in the current invention aim to primarily increase the reactivity or catalytic properties of the bauxite, not necessarily its surface area (surface area enhancement is generally the goal of common heat treatments at 400 °C or higher that result in the manufacture of products called activated bauxite or activated alumina). For example, wetting with water enhances the reactivity of the bauxite (without increasing its surface area) by depositing hydroxyl ions on the bauxite surface.

In the case of gaseous streams, an additional essential ingredient in the current invention is the presence of sulfur. The sulfur may already be

- 30 present in the target gas stream or may be introduced into the sequestration process, either through the gas stream or through addition to the bauxite.

consumed in large enough quantities, that they are available at reasonable cost. Other minerals useful with the invention include goethite, feldspar, and lignite. Typically, feldspar and lignite are contemplated for removal of mercury. Minerals, such as these, contain a variety of constituents that can react with pollutants and either adsorb or destroy them.

Example 1

The first pollutant that was tested was arsenic. There is a great deal of interest in arsenic, especially because a reduction in the regulatory limit for this pollutant in drinking water has recently been made. The limit (health standard in the U.S.) for arsenic in drinking water has been reduced from 50 µg/L to 10 µg/L.

The Table 1 shows the results of several batch tests. Batch tests were conducted in small bottles containing a locally obtained groundwater. Arsenic was spiked into the water to levels of approximately 1,400 µg/L.

The results show that arsenic levels in the water were reduced from approximately 1,400 µg/L to between about 19.8 µg/L and 86.4 µg/L when the mineral was added to the water and shaken on a shaker table for 24 hours. Nitrogen was bubbled through the water before the tests in order to remove dissolved oxygen and maintain the arsenic as As (III), versus As (V). The lower-valent arsenic is more difficult to treat and was considered a greater challenge for the test. The bottles were filled to the top with little or no headspace. After shaking, the bottles were centrifuged to settle out the mineral. The supernatant was then analyzed. The results are in the Table 1 below.

Table 1 - Treatment with raw minerals for groundwater containing arsenic

Test Sample	Arsenic Concentration (µg/L)	Removal
Initial Arsenic Concentration 1*	1,350	--
Initial Arsenic Concentration 2 *	1,420	--
Magnetite, Repetition 1	76.9	94%

5 **Table 2. Treatment of varying initial dissolved concentrations of arsenic with minerals**

Mineral	Initial Concentration ($\mu\text{g/L}$)	Day 1 ($\mu\text{g/L}$)	Day 2 ($\mu\text{g/L}$)	Removal (%)
Bauxite	85.7	< 10 < 10	< 10 < 10	> 88.3% >> 88.3%
	40.8	< 10 < 10	< 10 < 10	> 75.5% > 75.5%
	20.1	< 10 < 10	< 10 < 10	> 50.2% > 50.2%
	85.7	27.3 26.0	12.2 12.4	68.1% to 85.8% 69.7% to 85.5%
	40.8	13.2 < 10	< 10 < 10	67.6% to > 75.5% > 75.5%
	20.1	< 10 < 10	< 10 < 10	> 50.2% > 50.2%
Hematite	85.7	38.4	36.4	55.2% to 57.5%

When the bauxite test bottles were shaken (mixed) for one more day, there were no signs that any of the sequestered arsenic was desorbed or otherwise released from the solid mineral. The same was true for magnetite and hematite, after two days of shaking.

Hematite and magnetite were not as efficient as bauxite under all conditions, but still removed between 55% to over 99% of the arsenic under some conditions. All three minerals reduced arsenic to below 50 $\mu\text{g/L}$, the current regulatory limit.

Raw bauxite ore typically contains varying proportions of aluminum oxide (35% to 65% as gibbsite, boehmite, and/or diasporite), silica (0.5% to 10% as quartz and/or kaolinite) and iron oxide (2% to 30% as goethite, hematite, and/or siderite), titanium oxide (0.5% to 8% as anatasite and/or rutile), and calcium oxide (0 to 5% as calcite, dolomite, and/or magnetite).

Again not wishing to be bound by theory, it is presently believed that in

environmental conditions, bauxite and other minerals (like Al, Cu, Mn ores and minerals) generally carry a positive charge. The point of zero charge of bauxite generally occurs between a pH of 7.53 and 8.29, depending on the electrolyte concentration. The point of zero charge of other mineral oxides
5 are: α -Al₂O₃, γ -AlOOH, CuO, α -Fe₂O₃, are 9.1, 8.2, 9.4, and 8.6, respectively. These oxides, hydroxides, and other mixture of minerals are known for their oxidizing properties. Viral inactivation covers a wide range of phenomena, from mild, reversible inactivation (e.g., by non-specific sorption on quartz sand) to severe, irreversible fragmentation of viral proteins by lysis (e.g.,
10 exposure to strong oxidants, chemisorption, etc.). Coordination of carbonyl groups from peptide linkages of sorbed viruses at the mineral surfaces may provide a conduit of electron transfer. Viral die-off may occur in the presence of active chemical sites on these barrier materials by a variety of mechanisms, including:
15 (i) disruption of the virus membrane;
(ii) blockage of the receptor-ligand interactions essential for infectivity;
(iii) inhibition of the replication of pathogens; or
(iv) alteration of the environment and reduction of the susceptibility of infection.
20 Typically, in practice the emissions of power plants, industry, medical facilities, homes, or other point sources are contacted with the mineral ores described herein so that the pollutants in the emissions are adsorbed, absorbed, chemically reacted, or otherwise inactivated.
In one embodiment of the invention, a gas stream containing pollutant
25 metals passes through a bed of granular bauxite (see Figure 1). An essential ingredient of the current invention for the application to gas streams is the presence of sulfur. The geochemical complexation in these solid-phase surfaces generates sufficient sulfide/bisulfide to precipitate contaminants metals as insoluble sulfides for long-term remediation of impacted sites. The
30 thermodynamic parameters of the metal sulfides are given in Table 3. The low value of solubility product of metal sulfides indicates that these sulfides are very insoluble compound. Also, considering the Gibbs free energy (ΔG)

form, crushed to -8+50 mesh size range was used in this test. The presence of SO₂ in the gas stream facilitates the co-precipitation of mercury as a sulfide.

5 In a second embodiment of the invention the bauxite is introduced in a powdered form into the gas stream. In the powdered form, the bauxite is much more reactive with the SO₂ and metals. Also, injection of bauxite powder can be implemented without increasing the pressure drop (and energy requirement) in the flue gas equipment in a power plant. The
10 mercury would be recovered along with the fly ash. In a fixed bed of bauxite, additional pressure drop would be introduced into the flue gas system, but the mercury can be recovered separate from the fly ash. In either case, the mercury is in a much less bio-available form.

15 In a third embodiment, the bauxite is modified to enhance its sequestration capability while retaining its essential character. One modification that enhances sequestration is wetting of the bauxite surfaces with water. Other modifications include, but are not limited to, hydroxyl, sulfonyl, thiol moieties associated with the surface. These functional groups
20 improve the metal removal efficiency. The modifications will be limited to simple processes, such as soaking the bauxite in solutions of acids, bases, or salts. Any heat treatment will involve milder temperatures (300 °C) or less compared to the temperatures typically involved in manufacture of activated bauxite (400 °C or more).

25 In a fourth embodiment, the bauxite is applied in granular form as a permeable medium for the in situ treatment of groundwater (see Figure 3a and b). Sulfur is not an essential ingredient in the sequestration of pollutant metals in water or soil environments. Table 4 shows the results of
30 experiments conducted with groundwater containing mercury, arsenic, cadmium, and chromium. All these metals were substantially removed by the bauxite.

combination with aluminum tri-hydrate by the said others. However, heat treatment is energy intensive and expensive and is unnecessary for the current invention. In this embodiment of the current invention, where bauxite is applied as a permeable medium for in situ treatment of groundwater, high efficiency and high capacity are not as important as easy availability and low cost. This is because groundwater flows very slowly (typically 1 foot per day or less linear velocity). In this situation, the contact time available to the water as it flows through the bauxite medium is of the order of several hours or days. Because the bauxite material is cheap, it can be installed as a treatment medium that is several feet thick in the path of the groundwater flow to provide the longer contact times and to provide moderately high sequestration capacity. Bauxite can therefore be effectively applied in situations where slightly longer contact times can be arranged. Alternatively, in the current invention the reactivity of the bauxite may be modified or improved without heat treatment, for example, by soaking the bauxite in or wetting it with a solution of common acids, bases, or salts. This is a simpler and much less expensive modification than heat treatment.

In a fifth embodiment, the bauxite is applied as a cap over contaminated sediments under surface water bodies to prevent the migration of metal pollutants from the sediments to the water column above (see Figure 4a and b). Table 5 shows the results of experiments conducted with sediments from two sources, New York Harbor and Sequim. In each case, bauxite removed the pollutant metals substantially.

In a sixth embodiment, the bauxite is applied as a treatment for scrubber water exiting a power plant. In power plants that have scrubber, many of the heavy metals in the combustion gases are removed in the scrubber water and the water has to be treated before discharge. This water could be passed through a bed of granular bauxite. Alternatively, powdered bauxite could be added to the water and then separated out by settling or filtration.

In all these embodiments, bauxite, a relatively cheap sequestering agent is not regenerated and is applied as a single use reagent. This enhances the economic attractiveness of the treatment process. For example, during treatment of combustion gas streams, powdered bauxite is injected into the gas and the metals-laden bauxite is collected downstream with the fly ash. The bauxite and the sequestered metals are disposed or reused according to the ongoing convention at the plant. The metals being in a non-mobile, non-bio-available, sulfide form on the bauxite their subsequent potential leachability to the environment is very limited. The waste product (e.g., fly ash) can therefore be safely reused in a variety of products. In the case of treatment of groundwater or sediments, the bauxite can be permanently left in the environment after it has served its purpose.

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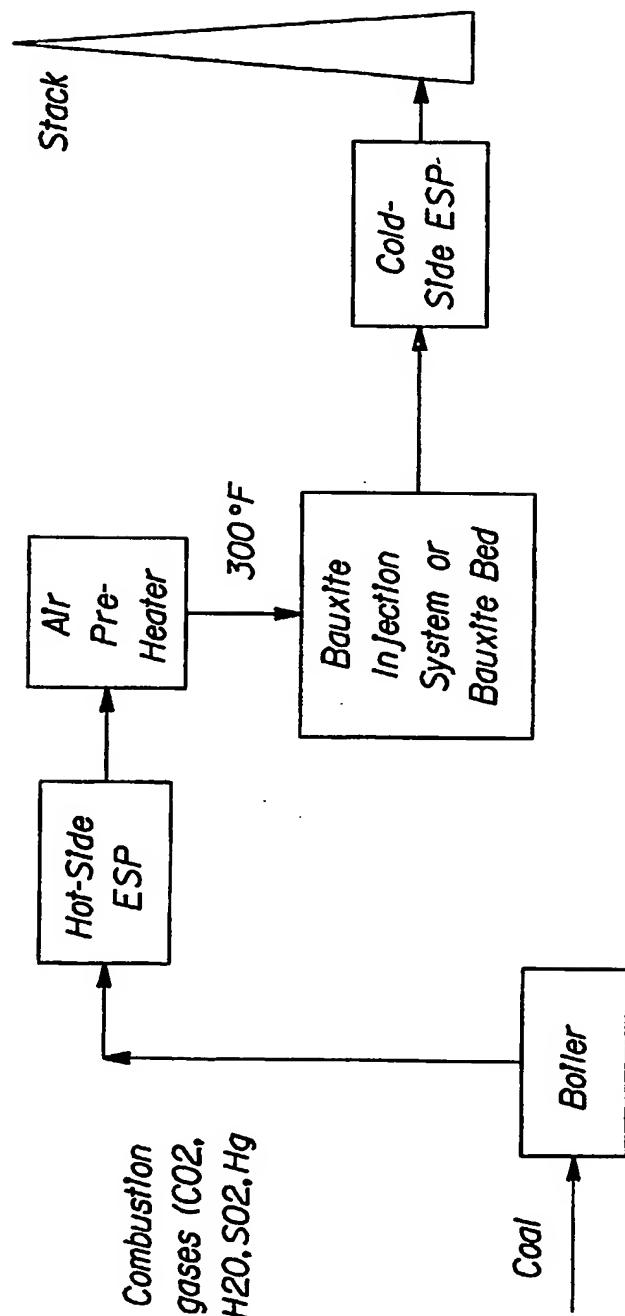


Fig. 1

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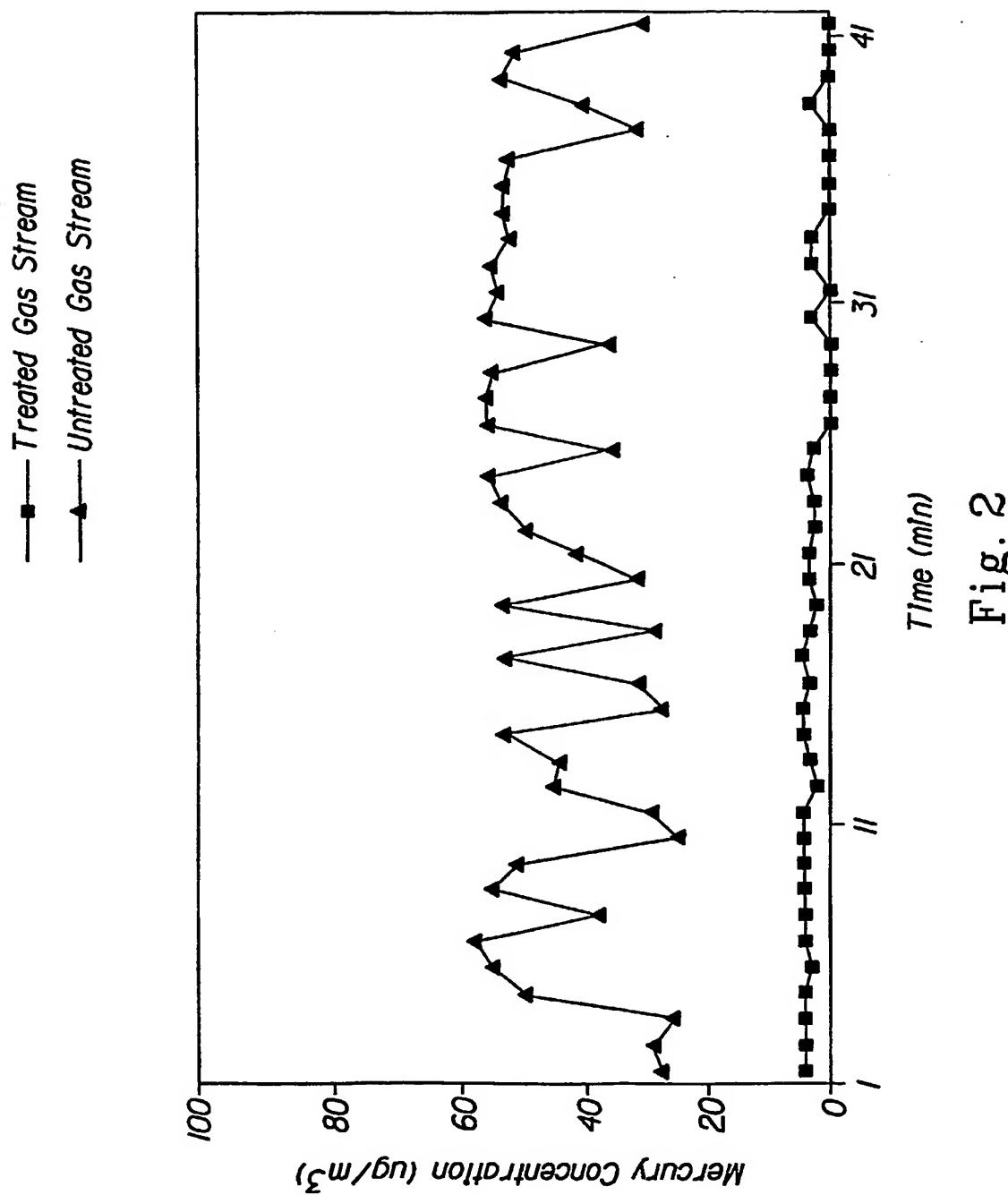


Fig. 2

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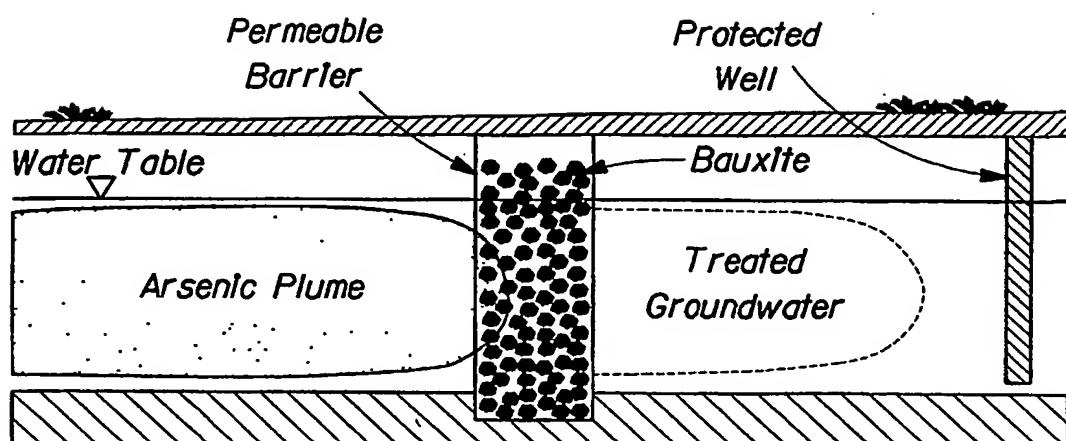


Fig. 3A

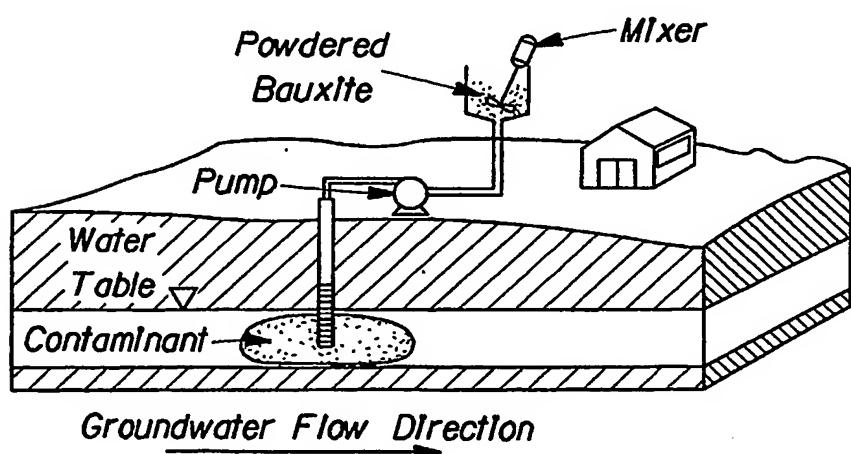


Fig. 3B

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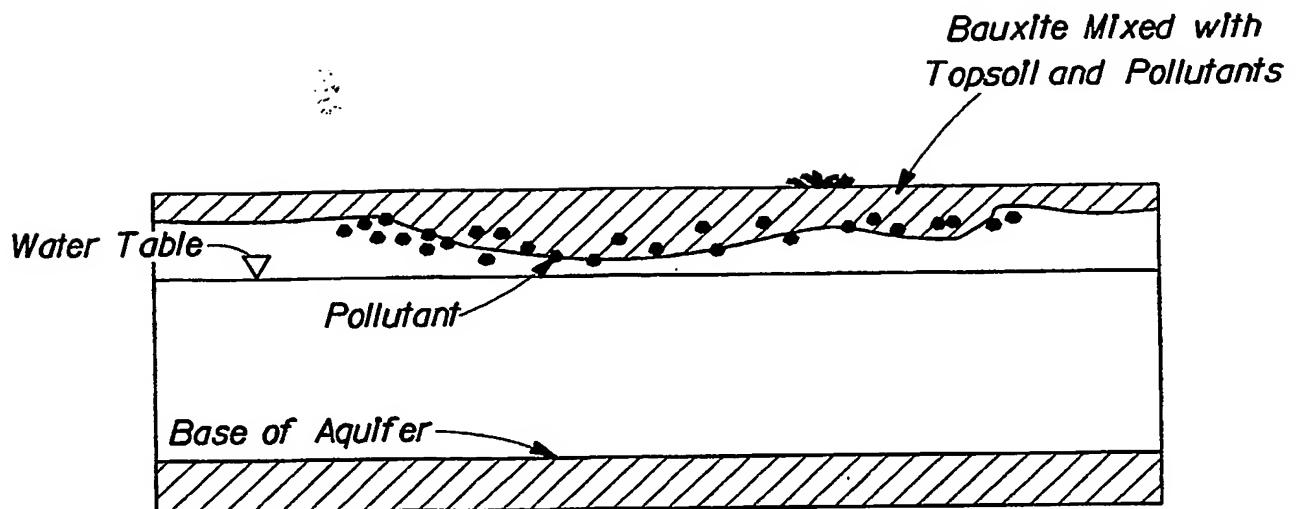


Fig. 4A

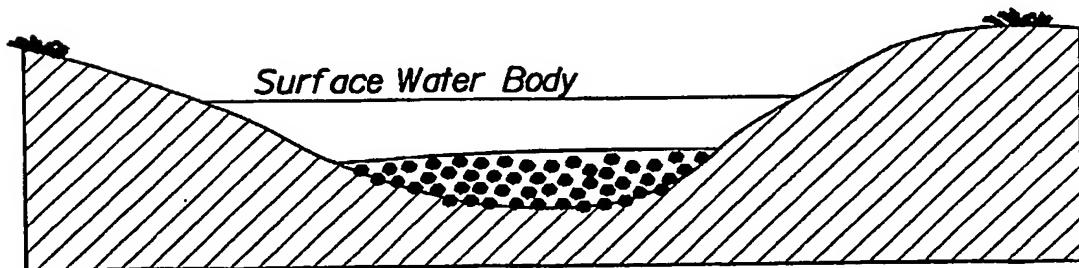


Fig. 4B

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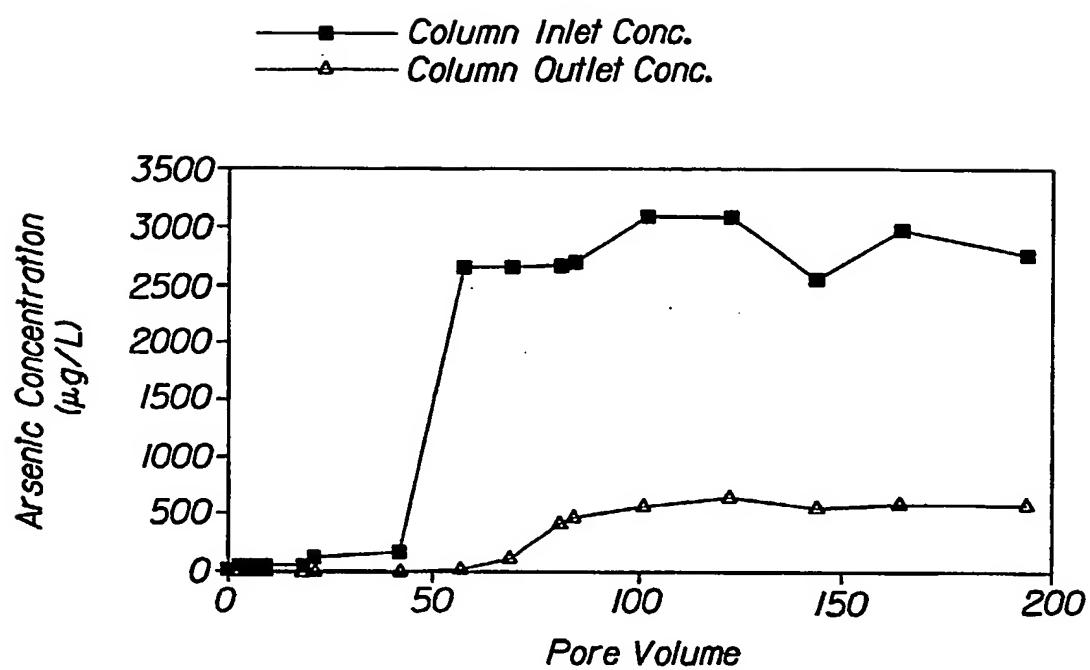


Fig. 5